

FORM PTO-1390 (Rev 10-95)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEYS DOCKET NO. 7095HL-1
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 35 CFR 1.5) 09/913324 ✓
INTERNATIONAL APPLICATION NO. PCT/RU99/00037 ✓	INTERNATIONAL FILING DATE 11 February 1999 ✓	PRIORITY DATE CLAIMED	
TITLE OF INVENTION "TUNGSTEN CARBIDE COATING AND METHOD FOR ITS PRODUCTION"			
APPLICANT(S) FOR DO/EO/US LAKHOTKIN, Jury Viktorovich and KUZMIN, Vladimir Petrovich			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)). <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 			
Items 11. To 16. below concern documents or information included:			
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.23 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input type="checkbox"/> Other items or information: 			
"EXPRESS MAIL" MAILING LABEL NUMBER: EL822581508US DATE OF DEPOSIT. August 10, 2001 I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED ABOVE AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, BOX PCT, WASHINGTON, D.C. 20231. TYPED OR PRINTED NAME: JANICE MESSER SIGNATURE: <i>Janice Messer</i>			

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SUBTOTAL =	\$ 1,352.00
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TOTAL FEES ENCLOSED =	\$	1,352.00
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Amount to be:	\$
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charged	\$
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PATENT APPLICATIONS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re the Application of:

LAKHOTKIN, Jury Viktorovich and
KUZMIN, Vladimir Petrovich

Int'l. Serial No.: PCT/RU99/00037

Int'l. Filing Date: 11 February 1999

Priority Date: None

For: "TUNGSTEN CARBIDE COATING AND
METHOD FOR ITS PRODUCTION"

Atty. File No.: 7095HL-1

Box PCT

Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Prior to the initial review of the above-identified patent application by the Examiner, please enter the following Preliminary Amendment. Fees for this Preliminary Amendment are calculated and included with the Transmittal Letter accompanying this Amendment. Please charge any underpayment or debit any overpayment to Deposit Account 19-1970.

Please amend the above-identified patent application as follows:

In the Specification:

On Page 7, Table 1, Column 4, line 1 please delete "Tngsten" and insert – Tungsten – as follows:

Table 1

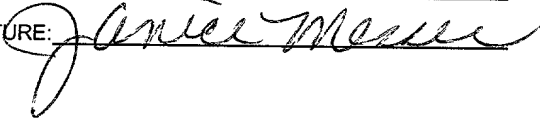
No.	Composition	Propane activation temperature, °C	Propane to hydrogen ratio	Tungsten hexafluoride to hydrogen ratio

PRELIMINARY AMENDMENT

"EXPRESS MAIL" MAILING LABEL NUMBER: EL822581508US
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TYPED OR PRINTED NAME: JANICE MESSER

SIGNATURE: 

Please replace the third paragraph on Page 14 (second paragraph of Example 5), line 16, with the following rewritten paragraph:

– The construction material thus obtained with tool steel with a layer of nickel as the base material has a composite coating with an internal tungsten (W) layer of thickness 1.3 μm and an external layer of W_2C of thickness 9.1 μm . The microhardness of the coating is 2800 kG/mm^2 . —

Please replace the third paragraph on Page 22 (second paragraph of Example 21), line 21, with the following rewritten paragraph:

The construction material thus obtained with tool steel R6M5 as the base material and an intermediate nickel layer 8 μm thick has a composite coating with 11 alternating layers of W and W_{12}C both with thickness 5 μm at a ratio of thicknesses 1:1 and total thickness of the composite coating 110 μm . The average microhardness of the coating is 2550 kG/mm^2 .

In the Claims:

Please cancel Claims 66 and 90.

Please amend Claims 8-50, 57-65, 67, 69-75 and 87-89 as follows:

8. (Amended) Coating, characterized in that it contains:

- an internal layer consisting of tungsten deposited on a substrate;
- and an external layer deposited on the said internal layer and containing tungsten carbide

in accordance with claim 1.

9. (Amended) Coating in accordance with claim 6, characterized in that its outer layer additionally contains a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possible with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

10. (Amended) Coating in accordance with claim 8, characterized in that its outer layer additionally contains tungsten.

11. (Amended) Coating in accordance with claim 8, characterized in that its outer layer additionally contains carbon.

12. (Amended) Coating in accordance with any of claim 8, characterized in that its internal layer has a thickness of 0.5-300 μm and its outer layer has a thickness of 0.5-300 μm , with the ratio of thicknesses of the internal and external layers ranging from 1:1 to 1:600.

13. (Amended) Process for producing tungsten carbides by chemical vapour deposition on a heated substrate using a mixture of gases including tungsten hexafluoride, hydrogen, a carbon-containing gas and, optionally, an inert gas, characterized in that the carbon-containing gas is thermally activated beforehand by heating to temperature 500-850°C.

14. (Amended) Process in accordance with claim 13, characterized in that the said carbon-containing gas is propane.

15. (Amended) Process in accordance with claim 13, characterized in that it is performed at a pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

16. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 1.0-1.5 and ratio of tungsten hexafluoride to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, tungsten monocarbide WC is obtained.

17. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.75-0.90 and ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, tungsten semicarbide W_2C is obtained.

18. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.05-0.55, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, tungsten subcarbide W_3C is obtained.

19. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.45 and ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, tungsten subcarbide $W_{12}C$ is obtained.

20. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.90-1.00 and ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, a mixture of the carbides WC and W_2C is obtained.

21. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.75 and ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated beforehand to temperature 580-730°C; in this case, a mixture of the carbides W_2C and W_3C is obtained.

22. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, a mixture of the carbides W_2C and $W_{12}C$ is obtained.

23. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.45-0.60 and ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, a mixture of the carbides W_3C and $W_{12}C$ is obtained.

24. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.65-0.70 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, a mixture of the carbides W_2C , W_3C and $W_{12}C$ is obtained.

25. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, a mixture of the carbide WC and tungsten is obtained.

26. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, a mixture of the carbides W_2C and tungsten is obtained.

27. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, a mixture of the carbide W_3C and tungsten is obtained.

28. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.20-0.35 and ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbide $W_{12}C$ and tungsten is obtained.

29. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.60 and ratio of tungsten hexafluoride to hydrogen 0.05-0.07, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbides W_3C , $W_{12}C$ and tungsten is obtained.

30. (Amended) Process in accordance with claim 15, characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 1.50-1.70 and ratio of tungsten hexafluoride to hydrogen 0.10-0.12, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, a mixture of the carbide WC and carbon is obtained.

31. (Amended) Process for the deposition of coatings consisting of an internal layer of tungsten and an external layer containing tungsten carbide on substrates, preferably on construction materials and on items made from them, characterized in that the said process includes the following stages:

- (a) placing the substrate in a chemical vapor deposition reactor;
- (b) evacuating the reactor;
- (c) heating the said substrate;
- (d) supplying tungsten hexafluoride and hydrogen to the reactor;

(e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;

(f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;

(g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbides and mixtures of them with each other, with tungsten or with free carbon.

32. (Amended) Process in accordance with claim 31, characterized in that it is performed at a reactor pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

33. (Amended) Process in accordance with claim 31, characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical deposition from aqueous solutions, electrolysis of melts or physical and chemical vapor deposition.

34. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 1.00-1.50 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, an external layer containing tungsten monocarbide WC is obtained.

35. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.75-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, an external layer containing tungsten semicarbide W_2C is obtained.

36. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to

hydrogen 0.050-0.055, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, an external layer containing tungsten subcarbide W_3C is obtained.

37. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.40 and a ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, an external layer containing tungsten monocarbide $W_{12}C$ is obtained.

38. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.90-1.00 and a ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, an external layer containing a mixture of the carbides WC and W_2C is obtained.

39. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.75 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated beforehand to temperature 580-730°C; in this case, an external layer containing a mixture of the carbides W_2C and W_3C is obtained.

40. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.65-0.70 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, an external layer containing a mixture of the carbides W_2C , W_3C and $W_{12}C$ is obtained.

41. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, an external layer containing a mixture of the carbides W_2C and $W_{12}C$ is obtained.

42. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.40-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ is obtained.

43. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide W_2C and tungsten is obtained.

44. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, an external layer containing a mixture of the carbide W_3C and tungsten is obtained.

45. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.050-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-690°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ with tungsten is obtained.

46. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.20-0.35 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, an external layer containing a mixture of the carbide $W_{12}C$ and tungsten is obtained.

47. (Amended) Process in accordance with claim 32, characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide WC and tungsten is obtained.

48. (Amended) Process in accordance with any of claim 31, characterized in that the coatings are deposited onto frictional assemblies.

49. (Amended) Process in accordance with any of claim 31, characterized in that the coatings are deposited onto forming tools used for processing materials by means of pressing.

50. (Amended) Process in accordance with any of claim 31, characterized in that the coatings are deposited onto components and units of machines and mechanisms operating with compressed gases and liquids or other pneumatic or hydraulic systems.

57. (Amended) Material in accordance with claim 56, characterized in that the external layer of the said coating contains a mixture of the tungsten carbides WC and W_2C .

58. (Amended) Material in accordance with claim 56, characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and W_2C .

59. (Amended) Material in accordance with claim 56, characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and $W_{12}C$.

60. (Amended) Material in accordance with claim 56, characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C and $W_{12}C$.

61. (Amended) Material in accordance with claim 56, characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C , W_3C and $W_{12}C$.

62. (Amended) Material in accordance with claim 52, characterized in that the external layer of the said coating additionally contains tungsten.

63. (Amended) Material in accordance with claim 52, characterized in that the external layer of the said coating additionally contains carbon.

64. (Amended) Material in accordance with claim 52, characterized in that the internal layer of the said coating has thickness $0.5-300\ \mu m$ and the ratio of thicknesses of internal and external layers ranges from 1:1 to 1:600.

65. (Amended) Material according to claim 52, characterized in that the said substrate layer adjacent to the coating contains alloys with nickel content exceeding 25 wt%, e.g. Invar, Nichrome, Monel.

67. (Amended) Multilaminar coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with claim 1.

69. (Amended) Multilaminar coating in accordance with claim 67, characterized in that the thickness of its individual layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

70. (Amended) Process for the deposition of multilaminar coatings on substrates, preferably on construction materials and items made from them, consisting of alternating layers of tungsten and layers containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten or with free carbon, said process to include the following stages:

- (a) (Amended) placing the substrate in a chemical vapor deposition reactor;
- (b) evacuating the reactor;
- (c) heating the said substrate;
- (d) supplying tungsten hexafluoride and hydrogen to the reactor;
- (e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;
- (f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;
- (g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten and with free carbon; stages (d) to (g) are repeated several times in order to form alternating layers of tungsten and layers containing tungsten carbides.

71. Process in accordance with claim 70, characterized in that it is conducted at reactor pressure 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

72. Process in accordance with claim 70, characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds

and mixtures of these, by electrochemical or chemical deposition from aqueous solutions, electrolysis of melts or physical and chemical vapor deposition.

73. Process in accordance with claim 70, characterized in that the coating is deposited onto friction assemblies.

74. Process in accordance with claim 70, characterized in that the coating is deposited onto a forming tool used for processing materials by means of pressing.

75. Process in accordance with claim 70, characterized in that the coating is deposited onto units of machines and mechanisms operating with compressed gases and liquids or of other pneumatic or hydraulic systems.

87. Material in accordance with claim 76, characterized in that the said carbide layers additionally contain tungsten.

88. Material in accordance with claim 76, characterized in that the said carbide layers additionally contain carbon.

89. Materials according to claim 76, characterized in that the thickness of its layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

REMARKS/ARGUMENTS

The above amendments are being submitted in connection with the national stage filing of the present Application. The amendments eliminate the multiple dependent claims and to place the Application more in compliance with the standards of the U.S. Patent Office.

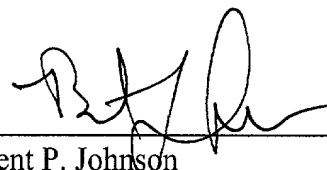
Express Mail #EL822581508US
Application No.: PCT/RU99/00037

Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned **"Version With Markings to Show Changes Made."**

Respectfully submitted,

SHERIDAN ROSS P.C.

By: _____


Brent P. Johnson
Registration No. 38,031
1560 Broadway, Suite 1200
Denver, Colorado 80202-5141
(303) 863-9700

Date: _____

8/9/01

VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

On Page 7, Table 1, Column 4, line 1, has been amended as follows:

Table 1

No.	Composition	Propane activation temperature, °C	Propane to hydrogen ratio	Tungsten hexafluoride to hydrogen ratio
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On Page 14, Paragraph 3, Example 5, has been amended as follows:

The construction material thus obtained with [copper] tool steel with a layer of nickel as the base material has a composite coating with an internal tungsten (W) layer of thickness 1.3 μm and an external layer of W_2C of thickness 9.1 μm . The microhardness of the coating is 2800 kG/mm^2 .

On Page 22, Paragraph 3, Example 21, has been amended as follows:

The construction material thus obtained with tool steel R6M5 as the base material and an intermediate nickel layer 8 μm thick has a composite coating with 11 alternating layers of W and W_{12}C both with thickness 5 μm at a ratio of thicknesses [1:11] 1:1 and total thickness of the composite coating 110 μm . The average microhardness of the coating is 2550 kG/mm^2 .

In the Claims:

Claims 66 and 90 have been canceled.

Claims 8-50, 57-65, 67, 69-75 and 87-89 have been amended as follows:

8. (Amended) Coating, [*characterised*] characterized in that it contains:

- an internal layer consisting of tungsten deposited on a substrate;
- and an external layer deposited on the said internal layer and containing tungsten carbide

in accordance with claim[s] 1[-6].

9. (Amended) Coating in accordance with claim 6, *[characterised]* characterized in that its outer layer additionally contains a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possible with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt% [in accordance with claim 7].

10. (Amended) Coating in accordance with claim[s] 8[or 9], *[characterised]* characterized in that its outer layer additionally contains tungsten.

11. (Amended) Coating in accordance with claim[s] 8[or 9], *[characterised]* characterized in that its outer layer additionally contains carbon.

12. (Amended) Coating in accordance with any of claim[s] 8[to 11], *[characterised]* characterized in that its internal layer has a thickness of 0.5-300 μm and its outer layer has a thickness of 0.5-300 μm , with the ratio of thicknesses of the internal and external layers ranging from 1:1 to 1:600.

13. (Amended) Process for producing tungsten carbides by chemical vapour deposition on a heated substrate using a mixture of gases including tungsten hexafluoride, hydrogen, a carbon-containing gas and, optionally, an inert gas, *[characterised]* characterized in that the carbon-containing gas is thermally activated beforehand by heating to temperature 500-850°C.

14. (Amended) Process in accordance with claim 13, *[characterised]* characterized in that the said carbon-containing gas is propane.

15. (Amended) Process in accordance with claim[s] 13[or 14], *[characterised]* characterized in that it is performed at a pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

16. (Amended) Process in accordance with claim 15, *[characterised]* characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 1.0-1.5 and ratio of tungsten hexafluoride to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, tungsten monocarbide WC is obtained.

17. (Amended) Process in accordance with claim 15, *[characterised]* characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.75-0.90 and ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, tungsten semicarbide W_2C is obtained.

18. (Amended) Process in accordance with claim 15, *[characterised]* characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.05-0.55, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, tungsten subcarbide W_3C is obtained.

19. (Amended) Process in accordance with claim 15, *[characterised]* characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.45 and ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, tungsten subcarbide $W_{12}C$ is obtained.

20. (Amended) Process in accordance with claim 15, *[characterised]* characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.90-1.00 and ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, a mixture of the carbides WC and W_2C is obtained.

21. (Amended) Process in accordance with claim 15, *[characterised]* characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.75 and ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated beforehand to temperature 580-730°C; in this case, a mixture of the carbides W_2C and W_3C is obtained.

22. (Amended) Process in accordance with claim 15, *[characterised]* characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, a mixture of the carbides W_2C and $W_{12}C$ is obtained.

23. (Amended) Process in accordance with claim 15, *[characterised]* characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.45-0.60 and ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, a mixture of the carbides W_3C and $W_{12}C$ is obtained.

24. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.65-0.70 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, a mixture of the carbides W_2C , W_3C and $W_{12}C$ is obtained.

25. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, a mixture of the carbide WC and tungsten is obtained.

26. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, a mixture of the carbides W_2C and tungsten is obtained.

27. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, a mixture of the carbide W_3C and tungsten is obtained.

28. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.20-0.35 and ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbide $W_{12}C$ and tungsten is obtained.

29. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.60 and ratio of tungsten hexafluoride to hydrogen 0.05-0.07, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbides W_3C , $W_{12}C$ and tungsten is obtained.

30. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 1.50-1.70 and ratio of tungsten hexafluoride to hydrogen 0.10-0.12, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, a mixture of the carbide WC and carbon is obtained.

31. (Amended) Process for the deposition of coatings consisting of an internal layer of tungsten and an external layer containing tungsten [subcarbide $W_{12}C$] carbide on substrates, preferably on construction materials and on items made from them, [*characterised*] characterized in that the said process includes the following stages:

- (a) placing the substrate in a chemical [vapour] vapor deposition reactor;
- (b) evacuating the reactor;
- (c) heating the said substrate;
- (d) supplying tungsten hexafluoride and hydrogen to the reactor;
- (e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;
- (f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;
- (g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbides and mixtures of them with each other, with tungsten or with free carbon.

32. (Amended) Process in accordance with claim 31, [*characterised*] characterized in that it is performed at a reactor pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

33. (Amended) Process in accordance with claim 31, [*characterised*] characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical [precipitation] deposition from aqueous solutions, electrolysis of melts or physical and chemical [vapour precipitation] vapor desposition.

34. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 1.00-1.50 and a ratio of tungsten

hexafluoride to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, an external layer containing tungsten monocarbide WC is obtained.

35. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.75-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, an external layer containing tungsten semicarbide W_2C is obtained.

36. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.050-0.055, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, an external layer containing tungsten subcarbide W_3C is obtained.

37. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.40 and a ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, an external layer containing tungsten monocarbide $W_{12}C$ is obtained.

38. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.90-1.00 and a ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, an external layer containing a mixture of the carbides WC and W_2C is obtained.

39. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.75 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated beforehand to temperature 580-730°C; in this case, an external layer containing a mixture of the carbides W_2C and W_3C is obtained.

40. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.65-0.70 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, an external layer containing a mixture of the carbides W_2C , W_3C and $W_{12}C$ is obtained.

41. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, an external layer containing a mixture of the carbides W_2C and $W_{12}C$ is obtained.

42. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.40-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ is obtained.

43. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide W_2C and tungsten is obtained.

44. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, an external layer containing a mixture of the carbide W_3C and tungsten is obtained.

45. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.050-0.070, and that the carbon-containing gas is heated beforehand to

temperature 500-690°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ with tungsten is obtained.

46. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.20-0.35 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, an external layer containing a mixture of the carbide $W_{12}C$ and tungsten is obtained.

47. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide WC and tungsten is obtained.

48. (Amended) Process in accordance with any of claim[s] 31[to 47], [*characterised*] characterized in that the coatings are deposited onto frictional assemblies.

49. (Amended) Process in accordance with any of claim[s] 31[to 47], [*characterised*] characterized in that the coatings are deposited onto forming tools used for processing materials by means of pressing.

50. (Amended) Process in accordance with any of claim[s] 31[to 47], [*characterised*] characterized in that the coatings are deposited onto components and units of machines and mechanisms operating with compressed gases and liquids or other pneumatic or hydraulic systems.

57. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides WC and W_2C [$W_{12}C$].

58. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and W_2C .

59. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and $W_{12}C$.

60. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C and $W_{12}C$.

61. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C , W_3C and $W_{12}C$.

62. (Amended) Material in accordance with claim[s] 52[-61], [*characterised*] characterized in that the external layer of the said coating additionally contains tungsten.

63. (Amended) Material in accordance with claim[s] 52[-61], [*characterised*] characterized in that the external layer of the said coating additionally contains carbon.

64. (Amended) Material in accordance with claim[s] 52[to 63], [*characterised*] characterized in that the internal layer of the said coating has thickness 0.5-300 μm and the ratio of thicknesses of internal and external layers ranges from 1:1 to 1:600.

65. (Amended) Material according to claim[s] 52[to 64], [*characterised*] characterized in that the said substrate layer adjacent to the coating contains alloys with nickel content exceeding 25 wt%, e.g. Invar, Nichrome, Monel.

67. (Amended) Multilaminar coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with [any of] claim[s] 1[to 6].

69. (Amended) Multilaminar coating in accordance with claim[s] 67[-68], [*characterised*] characterized in that the thickness of its individual layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

70. (Amended) Process for the deposition of multilaminar coatings on substrates, preferably on construction materials and items made from them, consisting of alternating layers of tungsten and layers containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten or with free carbon, said process to include the following stages:

- (a) (Amended) placing the substrate in a chemical [vapour] vapor deposition reactor;
- (b) evacuating the reactor;
- (c) heating the said substrate;
- (d) supplying tungsten hexafluoride and hydrogen to the reactor;

(e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;

(f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;

(g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten and with free carbon; stages (d) to (g) are repeated several times in order to form alternating layers of tungsten and layers containing tungsten carbides.

71. Process in accordance with claim 70, [*characterised*] characterized in that it is conducted at reactor pressure 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

72. Process in accordance with claim 70, [*characterised*] characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical [*precipitation*] deposition from aqueous solutions, electrolysis of melts or physical and chemical [*vapour precipitation*] vapor deposition.

73. Process in accordance with [any of] claim[s] 70[to 72], [*characterised*] characterized in that the coating is deposited onto friction assemblies.

74. Process in accordance with [any of] claim[s] 70[to 72], [*characterised*] characterized in that the coating is deposited onto a forming tool used for processing materials by means of pressing.

75. Process in accordance with [any of] claim[s] 70[to 72], [*characterised*] characterized in that the coating is deposited onto units of machines and mechanisms operating with compressed gases and liquids or of other pneumatic or hydraulic systems.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	

89. Materials according to [any of] claim[s] 76[to 88], [*characterised*] characterized in that the thickness of its layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

TUNGSTEN CARBIDE COATINGS AND
PROCESS FOR PRODUCING THEM

Technology field

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The invention is related to the technology of the deposition of composite surface systems possessing high resistance to wear, erosion and chemicals. More specifically, the invention is related to the technology of the deposition of coatings containing tungsten carbides and mixtures of them with each other and with tungsten or free carbon.

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Superhard erosion and corrosion resistant coatings, including those containing tungsten carbides, are widely used in manufacturing various articles and tools in present-day mechanical engineering. Such coatings possess high resistance to erosion, chemicals and wear, and thus substantially increase the life of mechanical engineering products and of tools operated under demanding conditions.

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Prior art

20 Patent GB 2 179 678 describes a surface composite system with high resistance to wear and erosion consisting of a mixture of tungsten (for plasticity) and tungsten carbide W_2C (for hardness). These hard coatings made from a fine-grain mixture of tungsten carbide with metallic tungsten were obtained by means of physical vapour deposition (PVD) by spraying tungsten and carbon from separate sources. The tungsten and carbon are condensed on different-type substrates to form the said alloys of tungsten with tungsten carbide.

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However, the rate of synthesis of tungsten carbides is very low, and internal stresses in the coatings increase sharply as the tungsten-carbon layer grows, resulting in delamination of the coatings. For this reason, it is impossible to produce sufficiently thick coatings by the PVD method. Furthermore, the physical vapour deposition

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method is intrinsically inapplicable for deposition of coatings on items of complex shape due to the impossibility of depositing the coatings on the parts of the item shadowed relative to the incident beam.

- 5 The chemical vapour deposition process (CVD) eliminates these disadvantages. The CVD process can be used to deposit wear and erosion resistant coatings on substrates and on items of complex shape.

In a typical CVD process for the deposition of composite coatings, the substrate is
 10 heated in the reaction chamber, and the previously mixed gas reagents are then introduced into this chamber. By varying the composition of the reaction mixture and of the parameters of the process (temperature of the substrate, composition of the reaction mixture, flow rate, total pressure in the reaction mixture, temperature of the gases supplied, etc.), it is possible to obtain a variety of coatings.

15 Among the CVD methods of tungsten carbide coating deposition, only the fluoride method makes it possible to form tungsten carbides of high quality at a low temperature. For this purpose, one may use thermal decomposition of a mixture of tungsten hexafluoride, hydrogen and carbon-containing gas in the CVD process.

20 Various reagents were used as carbon-containing gases, e.g. dimethylether, amines, propylene, etc., with the aid of which one may synthesise tungsten carbide of one or two compositions.

25 For example, the thermal decomposition of dimethylether (DME) (EP 0 328 084 B1) results in the formation of the mixture $W+W_3C$; $W+W_2C+W_3C$; $W+W_2C$ in the form of bilaminar coatings. The internal tungsten layer of the coating is obtained from the as mixture WF_6 (0.3 l/min), H_2 (3 l/min). Ar (4.0 l/min) at $460^\circ C$. The external layer containing a mixture of tungsten with W_3C is obtained from a mixture of WF_6 (0.3
 30 l/min), H_2 (3 l/min) and DME (0.4 l/min) at $460^\circ C$ at a total pressure of 40 torr. The external coating $W+W_2C$ is obtained from a mixture of WF_6 (0.3 l/min) and DME

(0.55 l/min) at 460°C at a total pressure of 40 torr. The external coating $W+W_2C$ is obtained from a mixture of WF_6 (0.3 l/min), Ar (4.5 l/min) and DME (0.85 l/min) at 460°C and a total pressure of 40 torr.

- 5 Patent JP 9113527 A 19910204 describes how tungsten carbide WC is obtained from a gaseous mixture of WF_6 , H_2 and amines with an atomic ratio of C to N equal to 1:20 and H to W equal to 1:15 at 400-900°C. The patent cites the production of WC from the mixture WF_6 :trimethylamine: H_2 =1:2:3 (the atomic ratios are $C/W = 6.0$, $H/W = 6.0$). The flow rate is 120 cm³/min at 800°C and the total pressure is equal to
10 atmospheric. A 70 µm layer forms in 30 minutes.

- Patent JP 8857301 A 19880310 describes how a W_3C coating on an aluminium substrate is obtained from a gaseous mixture of WF_6 , H_2 and aromatic hydrocarbon with atomic ratios C/W equal to 2-10 and H/C exceeding 3 at temperature 250-
15 500°C.

- Patent JP 84280063 A 19841228 describes how a W_2C coating on a graphite substrate is obtained from a gaseous mixture of WF_6 , C_3H_6 and H_2 with inert gas. The preferred regime: mixture WF_6 : H_2 =1:3-1:15 with an admixture of C_3H_6 in the
20 reaction mixture with molar ratio 0.01-0.3; the temperature of the substrate is 350-600°C.

- Patent JP 84204563 A 19840929 describes how a W_2C coating is obtained from a gaseous mixture of WF_6 , H_2 (molar ratio WF_6 : H_2 =1:3-1.15) and cyclopropane with
25 molar ratio in the mixture 0.01-0.3 at a substrate temperature of 350-600°C. The example cited is the manufacturing of a W_2C coating on a copper substrate from the mixture WF_6 : 40, H_2 : 320, Ar: 40, C_3H_8 : 10 cm³/min at 500°C with a growth rate of 3.3 µm/min.

- 30 EP A 0 305 917 describes how super-hard fine-grain non-columnar laminar tungsten-carbon alloys are obtained by chemical vapour deposition. The described alloys

contain carbide phases consisting of W_2C or W_3C or mixtures of them with each other. It is demonstrated that these tungsten carbon alloys, when deposited on certain types of substrate, have a net of very fine micro-cracks all over the deposit. Coatings made from these alloys have inadequate resistance to wear and erosion.

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EP 0 411 646 A1 describes a multilaminar coating containing alternating layers of tungsten and a mixture of tungsten with tungsten carbides in the form of W_2C , W_3C or a mixture of them. It is demonstrated that such a coating increases the resistance of the material to wear and erosion. It is known, however, that the maximum composition effect is observed for layers with a distinct boundary between them. This is obviously not the case for the conjunction of layers of tungsten and the mixture of tungsten with tungsten carbide which is characteristic of this patent.

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Substance of the invention

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It follows from the patents cited above that different reagents and different technologies are used for the production of different types of tungsten carbides. In this connection, the main aim of this invention is to develop a universal technology making it possible to obtain all the known carbides, mixtures of them and also new carbides.

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Furthermore, the problem of increasing the hardness of tungsten carbide coatings remains very important, because such key parameters as strength and wear resistance are related specifically to hardness.

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A solution to these and other problems is provided by this invention, due to the development of a new method for the production of tungsten carbides and mixtures of them. The main distinguishing feature of the method is the preliminary thermal activation of the hydrocarbons used in the CVD process. The synthesis of a tungsten carbide layer of a certain composition depends on an activation temperature that

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varies from 500 to 850°C, on a total pressure in the reactor that varies from 2 to 150 kPa, and on the partial pressure of the hydrocarbon reagent.

- Preliminary activation of the hydrocarbons results in the formation of the necessary concentration of hydrocarbon radicals and their associates with fluorine in the gaseous phase over a wide range. The proposed method makes it possible to alloy the carbides and/or mixtures of them with fluorine and fluoride-carbon compositions. Fluorine, as the most active chemical element, strengthens the interatomic bonds when it penetrates into the carbide lattice. It is the strengthening of the interatomic bonds in the carbide which produces the increase in hardness. This process is similar to the formation of oxycarbide phases instead of purely carbide structures. On the other hand, fluorine stabilises the structure of the low-temperature phases (tungsten subcarbides) due to the high energy of the fluorine-carbon bond.
- Along with fluorine as an element, fluorine-carbon compounds with carbon content up to 15 wt% and fluorine content up to 0.5 wt% can be introduced into the composition of the tungsten carbide. These admixtures have two roles: firstly, they increase the hardness of the tungsten carbides; and secondly, they stabilise the structure of the tungsten subcarbides. Thus, the introduction of fluorine and fluorine-carbon admixtures makes it possible to obtain such tungsten carbides as monocarbide WC, semicarbide W_2C and subcarbides W_3C and $W_{12}C$.

- The application of the new tungsten carbides makes it possible to manufacture a bilaminar coating, the internal layer of which (deposited on the substrate – a construction material or items made of it) is composed of tungsten. The external layer contains tungsten carbide alloyed with fluorine and possibly with fluorine-carbon compositions, or mixtures of such carbides with each other and also with tungsten and free carbon.
- The construction material with the deposited composition coating has an internal tungsten layer of thickness 0.5-300 μm . The thickness of the external layer is 0.5-

300 μm . The ratio of thicknesses of the internal and external layers ranges from 1:1 to 1:600.

In accordance with this invention, tungsten carbides are deposited in the chemical reactor on the substrate from a gaseous phase consisting of tungsten hexafluoride, hydrogen, a carbon-containing gas (e.g. propane), and, optionally, an inert gas (e.g. argon). The carbon-containing gas is thermally activated before being introduced into the reactor by heating it to 500-850°C. The pressure in the reactor ranges from 2 to 150 kPa. The substrate is heated to temperature 400-900°C. The ratio of carbon-containing gas to hydrogen ranges from 0.2 to 1.7, and the ratio of tungsten hexafluoride to hydrogen ranges from 0.02 to 0.12.

Within the stated limits, the parameters of the process are determined depending on which carbide or mixture of carbide with each other or with tungsten or with carbon is required to be produced. Thus, to produce tungsten monocarbide WC, the preliminary thermal activation of the carbon-containing gas is conducted at a temperature of 750-850°C. The ratio of propane to hydrogen is set in the interval 1.00-1.50, and the ratio of tungsten to hydrogen in the interval 0.08-0.10.

The corresponding parameters for the production of single-phase tungsten semicarbide W_2C are as follows: 600-750°C, 0.75-0.90 and 0.06-0.08. The parameters for the production of tungsten subcarbide W_3C are: 560-720°C, 0.60-0.65 and 0.050-0.055.

A previously unknown tungsten subcarbide, W_{12}C , with hardness 3500 kg/mm^2 , greater than that of any of the known carbides, was obtained by the method proposed in this invention. For the production of this subcarbide, propane was thermally activated at temperature 500-700°C. The ratio of propane to hydrogen was within the interval 0.35-0.40 and that of tungsten hexafluoride to hydrogen was 0.040-0.045.

This process makes it possible to obtain mixtures of tungsten carbides and mixtures of the carbides with free tungsten and carbon. The values of the parameters for these cases are shown in Table 1.

Table 1

No.	Composition	Propane activation temperature, °C	Propane to hydrogen ratio	Tungsten hexafluoride to hydrogen ratio
1.	WC+W ₂ C	670-790	0.90-1.00	0.07-0.09
2.	W ₂ C+W ₃ C	580-730	0.70-0.75	0.055-0.060
3.	W ₂ C+W ₁₂ C	570-700	0.60-0.65	0.045-0.060
4.	W ₃ C+W ₁₂ C	550-680	0.40-0.60	0.045-0.050
5.	W ₂ C+W ₃ C+W ₁₂ C	570-710	0.65-0.70	0.045-0.060
6.	WC+W	600-720	0.70-0.90	0.08-0.09
7.	W ₂ C+W	600-720	0.70-0.90	0.08-0.09
8.	W ₃ C+W	560-700	0.60-0.65	0.055-0.070
9.	W ₁₂ C+W	500-680	0.20-0.35	0.045-0.070
10.	W ₃ C+W ₁₂ C+W	500-680	0.35-0.60	0.05-0.07
11.	WC+C	750-850	1.50-1.70	0.10-0.12

5

As mentioned above, control of the content of active hydrocarbon radicals within wide limits is provided by means of the preliminary thermal activation of the initial carbon-containing reagent. This makes it possible to form carbide phases and mixtures of them with free carbon content of up to 15 wt%. The thermal activation of the carbon-containing reagent takes place in a hydrofluoric atmosphere, which provides additional formation of fluorine-carbon radicals. Radicals of both types take part in alloying the carbide phases and mixtures of them with fluorine and carbon, producing an increase in their hardness and enhanced tribotechnical properties.

15

Internal stresses increase slowly as the coatings of single-phase tungsten carbides grow; thus, high wear resistance is observed even with quite thick coatings (up to 300

μm). Their chemical resistance and high hardness are due to the strong interatomic bonds in the carbide lattice and the absence of free tungsten.

5 In order to bring about a microplastic effect in the coatings, one can use mixtures of carbides with each other and mixtures of them with tungsten and free carbon, in this case losing some chemical and electrochemical stability. Note that coatings of tungsten carbide with free carbon have a reduced friction coefficient in addition to the said microplastic effect. This is very important where mixtures of carbides with free carbon are used as wear-resistant tribotechnical coatings in friction assemblies.

10

By using the proposed invention and also the described new method of coating deposition, one can also obtain multilaminar coatings with alternating layers of tungsten and layers containing tungsten carbides alloyed with fluorine and possibly with fluorocarbon compositions, including mixtures of these carbides with each other and with tungsten or carbon. The ratio of thicknesses of the alternating layers ranges from 1:1 to 1:5.

15

The construction material itself, with a bilaminar or multilaminar coating deposited in accordance with the proposed method, is also an object of this invention.

20

Examples

Although the possibility of the application of the tungsten carbides obtained in accordance with the proposed invention on their own is not excluded, priority in their application is given to the deposition of these carbides as wear-resistant coatings on construction materials and items made of them. That is why the examples given below illustrate the invention specifically in cases of the deposition of carbides on substrates as coatings. However, these examples do not restrict the invention, because, for example, one can obtain other combinations of tungsten carbides with each other and/or tungsten and/or carbon.

25

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The examples given illustrate the production of complex coatings in which the layer of coating containing this or that tungsten carbide or mixtures of the carbides with each other and with tungsten and carbon is superimposed on a tungsten layer previously deposited on the substrate. The examples cover bilaminar coatings
 5 (internal layer of tungsten and external layer containing one or more tungsten carbides), and multilaminar coatings with alternating layers of tungsten and layers containing tungsten carbides.

The construction material on which the composite coating is deposited (or its
 10 external layer relative to the coating, in the case of bimetal) contains one of the following base materials: hard alloys, ceramics such as silicon carbide, silicon nitride, aluminium oxide, zirconium oxide, carbon-carbon composition materials etc., several iron-containing alloys such as iron, carbon steels, stainless steels, tool and high-speed steels and cast iron, or other materials from the following list: copper,
 15 silver, gold, cobalt, nickel, rhodium, rhenium, platinum, iridium, silicon, tantalum, niobium, vanadium, tungsten, molybdenum, carbon, nitrogen, boron, their alloys, compounds and mixtures, and also titanium alloys. The construction material or its outer layer adjacent to the coating should preferably consist of alloys with a nickel content exceeding 25 wt% e.g. Invar, Nichrome, Monel etc.

20 In the case of deposition onto chemically active materials such as iron, carbon steels, stainless steels, tool and high-speed steels, cast iron, titanium alloys and hard alloys containing titanium, it is preferable to deposit intermediate coatings containing materials chemically resistant to hydrogen fluoride, from the following list: copper,
 25 silver, gold, cobalt, nickel, rhodium, rhenium, platinum, iridium, tantalum, molybdenum, niobium, vanadium and boron. An intermediate coating of thickness 0.5-20 μm is deposited by electrochemical or chemical deposition from aqueous solutions, melt electrolysis, chemical or physical vapour deposition (e.g. by means of magnetron spraying) or by other methods.

30

The intermediate coatings thus obtained must be heat-treated at temperature 400-900°C for 0.5-1 hours in a flow of hydrogen or inert gas.

In the case of deposition onto materials chemically resistant to hydrogen fluoride, such as copper, silver, gold, cobalt, nickel, rhodium, rhenium, platinum, iridium, tantalum, molybdenum, tungsten, niobium, graphite, carbides or ceramics, intermediate coatings are not deposited. Various items of complex shape made from the material of the proposed composite coatings are manufactured by means of its deposition onto copper, silver, gold, cobalt, nickel, rhodium, rhenium, platinum, iridium, tantalum, molybdenum, tungsten, niobium or graphite, with subsequent removal of the substrate by chemical or electrochemical pickling or by other methods.

The substrates, degreased and free of contaminations, are put inside a direct-flow chemical reactor with an electric heater. The chemical reactor is evacuated by means of a roughing pump with a liquid nitrogen freezing trap up to maximum vacuum, after which hydrogen or argon is supplied to the reactor. The reactor with the items in it is then heated to the required temperature, which is maintained for 0.5-1 hours. After this, the required hydrogen flow rate and total pressure in the reactor are set. The required flow rate of tungsten hexafluoride, heated beforehand to 30°C, is then set. After the retention of the items in the set conditions for the time necessary for the application of the internal tungsten layer, the required total pressure is set and a certain flow rate of the carbon-containing gas (e.g. propane), previously heated to the required temperature, into the reaction mixture is set. A multilaminar composition coating is obtained by repeating the operation. After that, the supply of gas is terminated and the substrates are kept at constant temperature for 0.5-1 hours. After this stage, the temperature of the reactor is decreased to room temperature with hydrogen or argon being continuously supplied. The supply of hydrogen or argon is then terminated, the reactor is evacuated to maximum vacuum, and air is then admitted to it. The substrates with composite coatings are then removed from the reactor. Specific examples of the described method of deposition of a composite

coating are described below. The tests for hardness and for determining the phase composition of the coating were carried out in the following manner.

Hardness tests

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Hardness tests were conducted using a PMT-3 instrument. Samples made from steel or hard alloys with the composite coating applied were cut across. The cut was then ground with emery cloth and polished with diamond paste to maximum smoothness. The microhardness of the coatings was determined by pressing the pyramid-shaped diamond micro-indenter of the PMT-3 instrument into the middle of the external or internal layer of the composite coating at the polished cross-cut of the sample. The results were averaged over 7-10 measurements. It was determined from them that the microhardness of the internal tungsten layer was 350-600 kG/mm², the microhardness of tungsten monocarbide (WC) was 1900 kG/mm², the microhardness of tungsten semicarbide (W₂C) was 3000 kG/mm² and the microhardness of tungsten subcarbide W₃C was 3100 kG/mm². The new tungsten subcarbide W₁₂C possesses the greatest microhardness – 3500 kG/mm². Mixtures of tungsten carbides have intermediate hardness values.

20 Multilaminar coatings possessed medium hardness. In this case, the force on the diamond pyramid was selected so that the imprint extended into not less than four layers of the multilaminar coating. These hardness measurements were also repeated 7-10 times.

25 Determining the phase composition of the composite coating

The phase composition of the deposits was determined by means of X-ray and electron diffraction methods. X-ray studies were carried out using a DRON-3 diffractometer, with the use of copper radiation on flat samples of size 10×10 mm.

30 Qualitative phase analysis of the phases W, WC, W₂C, W₃C, W₁₂C and C was carried out by identifying the reflection lines, using ASTM data. The study of the

phase content of the compositions of tungsten carbides with free carbon was also carried out using illuminating electron microscopy. Furthermore, the determining of the phase content was supplemented by the chemical analysis of the total content of tungsten, carbon and fluorine. For this purpose, the external layer of the coating was removed from the copper substrate by dissolving the substrate in nitric acid and crushing the remaining coating substance. Its composition was then determined by analytical chemistry methods.

Example 1.

10

A sample made from carbon steel (Steel 3 in the Russian classification) with a layer of nickel of thickness 8 μm deposited on it by the electrochemical method is retained in a furnace at temperature 900°C in a medium of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.12 for 5 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.12 and a ratio of C_3H_8 to H_2 equal to 1.8 for 60 min; the C_3H_8 is thermally activated beforehand at 850°C and the reaction mixture pressure is 2 kPa.

20

The material obtained with Steel 3 as the base material has an intermediate 8- μm -thick nickel layer and a composite coating with an internal tungsten (W) layer of thickness 5 μm and an external layer (mixture of WC and free carbon [carbon black]) of thickness 40 μm . The microhardness of the coating is 840 kG/mm^2 . The coating has coarse inclusions of carbon black.

Example 2.

A sample made from stainless steel (Kh18N10T) with a layer of nickel of thickness 10 μm deposited on it by the electrochemical method is retained in a furnace at temperature 800°C in a medium of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.11 for 5 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio

of WF_6 to H_2 equal to 0.11 and a ratio of C_3H_8 to H_2 equal to 1.6 for 60 min; the C_3H_8 was activated beforehand at 840°C and the reaction mixture pressure is 8.8 kPa. The material obtained with stainless steel (Kh18N10T) as the base material has an intermediate 10- μm -thick nickel layer and a composite coating with an internal tungsten (W) layer of thickness 5 μm and an external layer (mixture of WC and free carbon) of thickness 35 μm . The microhardness of the coating is 1150 kG/mm^2 .

Example 3.

A sample made from stainless steel (Kh18N10T) with a layer of nickel of thickness 7 μm deposited on it by the electrochemical method is retained in a furnace at temperature 700°C in a medium of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.085 for 1 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.085 and a ratio of C_3H_8 to H_2 equal to 1.2 for 2.0 min; the C_3H_8 is thermally activated beforehand at 770°C and the reaction mixture pressure is 5.2 kPa.

The construction material thus obtained with stainless steel (Kh18N10T) as the base material has an intermediate 7- μm -thick nickel layer and a composite coating with an internal tungsten (W) layer of thickness 0.7 μm and an external WC layer of thickness 8 μm . The microhardness of the coating is 1900 kG/mm^2 .

Example 4.

A sample made from hard alloy VK-10 is retained in the reaction chamber at temperature 650°C in a medium of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.08 for 1 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.08 and a ratio of C_3H_8 to H_2 equal to 0.95 for 80 min; the C_3H_8 is thermally activated beforehand at 730°C and the reaction mixture pressure is 8.8 kPa.

The construction material thus obtained with hard alloy VK-10 as the base material has a composite coating with an internal tungsten (W) layer of thickness 0.7 μm and an external layer (mixture of W_2C and WC) of thickness 32 μm . The microhardness of the coating is 2800 kG/mm^2 .

5

Example 5.

A sample made from tool steel (3Kh2V8F) with a layer of nickel of thickness 5 μm deposited on it by the electrochemical method is retained in the reaction chamber at temperature 600°C in a medium of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.08 for 2 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.08 and a ratio of C_3H_8 to H_2 equal to 0.80 for 30 min; the C_3H_8 is thermally activated beforehand at 700°C and the reaction mixture pressure is 8.8 kPa. Chemical analysis showed that the fluorine content was $5 \cdot 10^{-2}$ wt%.

15

The construction material thus obtained with copper as the base material has a composite coating with an internal tungsten (W) layer of thickness 1.3 μm and an external layer of W_2C of thickness 9.1 μm . The microhardness of the coating is 2800 kG/mm^2 .

20

Example 6.

A sample made from tool steel R18 with a layer of nickel 5 μm thick applied to it by the electrochemical method is retained in the reaction chamber at temperature 550°C in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.057 for 5 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.057 and a ratio of C_3H_8 to H_2 equal to 0.67 for 70 min; the C_3H_8 is thermally activated beforehand at 640°C and the reaction mixture pressure is 5.2 kPa. The construction material thus obtained with steel R18 as the base material has an intermediate 5- μm nickel layer and a composite coating with an internal tungsten (W)

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layer of thickness 3 μm and an external layer (mixture of W_2C and W_3C) of thickness 25 μm . The microhardness of the coating is 2950 kG/mm^2 .

Example 7.

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A sample made from tool steel Kh12F1 with a layer of nickel 7 μm thick applied to it by the electrochemical method is retained in the reaction chamber at temperature 540°C in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.053 for 2 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.053 and a ratio of C_3H_8 to H_2 equal to 0.63 for 40 min; the C_3H_8 is thermally activated beforehand at 635°C and the reaction mixture pressure is 28 kPa.

10

The construction material thus obtained with tool steel Kh12F1 as the base material has a composite coating with a 7 μm nickel layer, then an internal tungsten (W) layer of thickness 1.0 μm and an external W_3C layer of thickness 18 μm . The microhardness of the coating is 3120 kG/mm^2 .

15

Example 8.

A sample made from tool steel R6M5 with a layer of nickel 5 μm thick applied to it by the electrochemical method is retained in the reaction chamber at temperature 520°C in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.045 for 5 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.045 and a ratio of C_3H_8 to H_2 equal to 0.60 for 180 min; the C_3H_8 is thermally activated beforehand at 610°C and the reaction mixture pressure is 42 kPa.

25

The construction material thus obtained with tool steel R6M5 as the base material has an intermediate 5 μm nickel layer, and a composite coating with an internal tungsten (W) layer of thickness 3 μm and an external layer (mixture of W_3C and W_{12}C) of thickness 100 μm . The microhardness of the coating is 3400 kG/mm^2 .

30

Example 9.

5 A sample made from tool steel 3Kh2V8F with a layer of nickel 5 μm thick applied to it by the electrochemical method is retained in the reaction chamber at temperature 520°C in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.044 for 2 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.044 and a ratio of C_3H_8 to H_2 equal to 0.4 for 160 min; the C_3H_8 is thermally activated beforehand at 600°C and the reaction mixture pressure is 28 kPa.

10

The construction material thus obtained with tool steel 3Kh2V8F as the base material has an intermediate 5 μm nickel layer, and a composite coating with an internal tungsten (W) layer of thickness 1 μm and an external W_{12}C layer of thickness 78 μm . The microhardness of the coating is 3500 kg/mm^2 .

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Example 10.

20 A sample made from stainless steel 2Kh13 with a layer of nickel 10 μm thick applied to it by the electrochemical method is retained in the reaction chamber at temperature 520°C in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.070 for 4 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.070 and a ratio of C_3H_8 to H_2 equal to 0.20 for 60 min; the C_3H_8 is thermally activated beforehand at 650°C and the reaction mixture pressure is 8.8 kPa.

25 The construction material thus obtained with stainless steel 2Kh13 as the base material has a composite coating with an internal tungsten (W) layer of thickness 3.8 μm and an external layer (mixture of W_{12}C and W) of thickness 20 μm . The microhardness of the coating is 2150 kg/mm^2 .

30

Example 11.

5 A sample made from "Monel" alloy is retained in the reaction chamber at temperature 580°C in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.085 for 3 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.085 and a ratio of C_3H_8 to H_2 equal to 0.80 for 60 min; the C_3H_8 is thermally activated beforehand at 680°C and the reaction mixture pressure is 8.8 kPa.

10

The construction material thus obtained with "Monel" alloy as the base material has a composite coating with an internal tungsten (W) layer of thickness 3.5 μm and an external layer (mixture of W_2C and W) of thickness 35 μm . The microhardness of the coating is 1740 kg/mm^2 .

15

Example 12.

20 A sample made from Invar alloy K6N38F is retained in the reaction chamber at temperature 590°C in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.063 for 3 min and then in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.063 and a ratio of C_3H_8 to H_2 equal to 0.63 for 40 min; the C_3H_8 is thermally activated beforehand at 630°C and the reaction mixture pressure is 8.8 kPa.

25 The construction material thus obtained with Invar alloy K6N38F as the base material has a composite coating with an internal tungsten (W) layer of thickness 3 μm and an external layer (mixture of W_3C and W) of thickness 19 μm . The microhardness of the coating is 1690 kg/mm^2 .

30

Example 13.

5 A sample made from a cake of natural diamonds is retained in the reaction chamber at temperature 520°C in a mixture of tungsten hexafluoride (WF₆) and hydrogen (H₂) at ratio 0.048 for 1 min and then in a medium of WF₆, H₂ and propane (C₃H₈) at a ratio of WF₆ to H₂ equal to 0.048 and a ratio of C₃H₈ to H₂ equal to 0.65 for 48 min; the C₃H₈ is thermally activated beforehand at 700°C and the reaction mixture pressure is 42 kPa.

10

The construction material thus obtained with a cake of natural diamonds as the base material has a composite coating with an internal tungsten (W) layer of thickness 0.8 μm and an external layer (mixture of W₂C and W₁₂C) of thickness 12 μm. The microhardness of the coating is 3220 kG/mm².

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Example 14.

20 A sample made from Nichrome alloy is retained in the reaction chamber at temperature 560°C in a mixture of tungsten hexafluoride (WF₆) and hydrogen (H₂) at ratio 0.070 for 8 min and then in a medium of WF₆, H₂ and propane (C₃H₈) at a ratio of WF₆ to H₂ equal to 0.070 and a ratio of C₃H₈ to H₂ equal to 0.2 for 40 min; the C₃H₈ is thermally activated beforehand at 650°C and the reaction mixture pressure is 5.2 kPa.

25 The construction material thus obtained with Nichrome alloy as the base material has a composite coating with an internal tungsten (W) layer of thickness 7 μm and an external layer (mixture of W and C) of thickness 41 μm. The microhardness of the coating is 1210 kG/mm².

30 **Examples of alternating layers.**

Example 15.

- A sample made from hard alloy VK6 is retained in the reaction chamber at temperature 620°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.08 for 2 min and then (b) in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.08 and a ratio of C_3H_8 to H_2 equal to 1.5 for 16 min; the C_3H_8 is thermally activated beforehand at 750°C and the reaction mixture pressure is 5.2 kPa. Operations (a) and (b) are repeated four times in succession.
- 10 The fluorine content in the multilaminar coating is $9 \cdot 10^{-3}$ wt%.

- The construction material thus obtained with hard alloy VK6 as the base material has a composite coating with four alternating layers of W with thickness 3.0 μm and of WC with thickness 7.0 μm at a ratio of thicknesses 1:2.3 and total thickness of the composite coating 40 μm . The average microhardness of the coating is 1320 kG/mm^2 .
- 15

Example 16.

- 20 A sample made from hard alloy VK10 is retained in the reaction chamber at temperature 650°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.08 for 1 min and then (b) in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.08 and a ratio of C_3H_8 to H_2 equal to 0.95 for 80 min; the C_3H_8 is thermally activated beforehand at 730°C and the reaction mixture pressure is 8.8 kPa. Operations (a) and (b) are repeated four times in succession.
- 25

- The construction material thus obtained with hard alloy VK10 as the base material has a composite coating with four alternating layers of W with thickness 0.7 μm and of a mixture of WC and W_2C with thickness 32 μm at a ratio of thicknesses 1:45.7 and total thickness of the composite coating 130.8 μm . The average microhardness of the coating is 2200 kG/mm^2 .
- 30

Example 17.

A sample made from tool steel 3Kh2V8F with a layer of nickel 5 μm thick deposited
 5 on it by the electrochemical method is retained in the reaction chamber at
 temperature 600°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen
 (H_2) at ratio 0.080 for 2 min and then (b) in a medium of WF_6 , H_2 and propane
 (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.080 and a ratio of C_3H_8 to H_2 equal to 0.7
 for 25 min; the C_3H_8 is thermally activated beforehand at 700°C and the reaction
 10 mixture pressure is 8.8 kPa. Operations (a) and (b) are repeated five times in
 succession.

The construction material thus obtained with tool steel 3Kh2V8F as the base material
 has a composite coating with five alternating layers of W with thickness 1.5 μm and
 15 W_2C with thickness 7.5 μm at a ratio of thicknesses 1:5 and total thickness of the
 composite coating 45 μm . The average microhardness of the coating is 2340
 kG/mm^2 .

Example 18.

20 A sample made from Invar alloy K6N38F is retained in the reaction chamber at
 temperature 580°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen
 (H_2) at ratio 0.060 for 5 min and then (b) in a medium of WF_6 , H_2 and propane
 (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.060 and a ratio of C_3H_8 to H_2 equal to 0.70
 25 for 40 min; the C_3H_8 is thermally activated beforehand at 650°C and the reaction
 mixture pressure is 8.8 kPa. Operations (a) and (b) are repeated 12 times in
 succession.

The construction material thus obtained with Invar alloy K6N38F as the base
 30 material has a composite coating with 12 alternating layers of W with thickness 3.0
 μm and a mixture of W_2C and W_3C with thickness 15.1 μm at a ratio of thicknesses

1:5 and total thickness of the composite coating 217 μm . The average microhardness of the coating is 2150 kG/mm^2 .

Example 19.

5

A sample made from tool steel Kh12F1 with a layer of nickel of thickness 7 μm deposited on it by the electrochemical method is retained in the reaction chamber at temperature 540°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.053 for 3 min and then (b) in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.053 and a ratio of C_3H_8 to H_2 equal to 0.62 for 27 min; the C_3H_8 is thermally activated beforehand at 635°C and the reaction mixture pressure is 28 kPa. Operations (a) and (b) are repeated five times in succession.

10

15

The construction material thus obtained with tool steel Kh12F1 as the base material has a composite coating with five alternating layers of W with thickness 5 μm and W_3C with thickness 12 μm at a ratio of thicknesses 1:264 and total thickness of the composite coating 85 μm . The average microhardness of the coating is 2250 kG/mm^2 .

20

Example 20.

A sample made from carbon steel 45 with a layer of nickel of thickness 6 μm deposited on it by the electrochemical method is retained in the reaction chamber at temperature 540°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.047 for 9 min and then (b) in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.047 and a ratio of C_3H_8 to H_2 equal to 0.55 for 150 min; the C_3H_8 is thermally activated beforehand at 630°C and the reaction mixture pressure is 5.2 kPa. Operations (a) and (b) are repeated seven times in succession.

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The construction material thus obtained with carbon steel 45 as the base material with an intermediate nickel layer 6 μm thick has a composite coating with seven alternating layers of W with thickness 4 μm and of a mixture of W_3C and W_{12}C with thickness 44 μm at a ratio of thicknesses 1:11 and total thickness of the composite coating 396 μm . The average microhardness of the coating is 2900 kG/mm^2 .

Example 21.

A sample made from tool steel R6M5 with a layer of nickel of thickness 3 μm deposited on it by the electrochemical method is retained in the reaction chamber at temperature 520°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.050 for 8 min and then (b) in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.043 and a ratio of C_3H_8 to H_2 equal to 0.35 for 11 min; the C_3H_8 is thermally activated beforehand at 650°C and the reaction mixture pressure is 8,8 kPa. Operations (a) and (b) are repeated 11 times in succession.

The construction material thus obtained with tool steel R6M5 as the base material and an intermediate nickel layer 8 μm thick has a composite coating with 11 alternating layers of W and W_{12}C both with thickness 5 μm at a ratio of thicknesses 1:11 and total thickness of the composite coating 110 μm . The average microhardness of the coating is 2550 kG/mm^2 .

Example 22.

A sample made from titanium alloy VT1 with a layer of nickel of thickness 1 μm deposited on it by magnetron spraying is retained in the reaction chamber at temperature 600°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.045 for 4 min and then (b) in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.045 and a ratio of C_3H_8 to H_2 equal to 0.65 for 60 min; the C_3H_8 is thermally activated beforehand at 600°C and the reaction

mixture pressure is 42 kPa. Operations (a) and (b) are repeated 15 times in succession.

The construction material thus obtained with titanium alloy VT1 as the base material
 5 has a composite coating with 15 alternating layers of W with thickness 5.2 μm and of
 a mixture of W_2C and W_{12}C with thickness 20 μm at a ratio of thicknesses 1:3.8 and
 total thickness of the composite coating 378 μm . The average microhardness of the
 coating is 2220 kG/mm^2 .

10 **Example 23.**

A sample made from nitride-silicon ceramics is retained in the reaction chamber at
 temperature 510°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen
 (H_2) at ratio 0.045 for 1 min and then (b) in a medium of WF_6 , H_2 and propane
 15 (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.045 and a ratio of C_3H_8 to H_2 equal to 0.35
 for 50 min; the C_3H_8 is thermally activated beforehand at 520°C and the reaction
 mixture pressure is 42 kPa. Operations (a) and (b) are repeated 12 times in
 succession. Chemical analysis showed that the fluorine content was $3.0 \cdot 10^{-1}$ wt%.

20 The construction material thus obtained with nitride-silicon ceramics as the base
 material has a composite coating with 12 alternating layers of W with thickness 0,7
 μm and of a mixture of W and W_{12}C with thickness 16 μm at a ratio of thicknesses
 1:22.8 and total thickness of the composite coating 204 μm . The average
 microhardness of the coating is 2220 kG/mm^2 .

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Example 24.

A sample made from titanium alloy VT1 with a layer of nickel of thickness 2 μm
 deposited on it by magnetron spraying is retained in the reaction chamber at
 30 temperature 600°C (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen
 (H_2) at ratio 0.09 for 3 min and then (b) in a medium of WF_6 , H_2 and propane (C_3H_8)

at a ratio of WF_6 to H_2 equal to 0.09 and a ratio of C_3H_8 to H_2 equal to 0.7 for 40 min; the C_3H_8 is thermally activated beforehand at $720^\circ C$ and the reaction mixture pressure is 5.2 kPa. Operations (a) and (b) are repeated seven times in succession.

- 5 The construction material thus obtained with titanium alloy VT1 as the base material has an intermediate nickel layer $2\text{ }\mu m$ thick and a composite coating with seven alternating layers of W with thickness $4.2\text{ }\mu m$ and of a mixture of W and W_2C with thickness $21.5\text{ }\mu m$ at a ratio of thicknesses 1:5.1 and total thickness of the composite coating $179.9\text{ }\mu m$. The average microhardness of the coating is 1830 kG/mm^2 .

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Example 25.

- A sample made from tool steel 3Kh3M3F with a layer of nickel of thickness $6\text{ }\mu m$ deposited on it by the electrochemical method is retained in the reaction chamber at
 15 temperature $500^\circ C$ (a) in a mixture of tungsten hexafluoride (WF_6) and hydrogen (H_2) at ratio 0.055 for 3 min and then (b) in a medium of WF_6 , H_2 and propane (C_3H_8) at a ratio of WF_6 to H_2 equal to 0.055 and a ratio of C_3H_8 to H_2 equal to 0.65 for 120 min; the C_3H_8 is thermally activated beforehand at $560^\circ C$ and the reaction mixture pressure is 8.8 kPa. Operations (a) and (b) are repeated four times in
 20 succession.

- The construction material thus obtained with tool steel 3Kh3M3F as the base material has a composite coating with four alternating layers of W with thickness $3.8\text{ }\mu m$ and of a mixture of W and W_3C with thickness $44.1\text{ }\mu m$ at a ratio of thicknesses
 25 1:11.6 and total thickness of the composite coating $191.6\text{ }\mu m$. The average microhardness of the coating is 1320 kG/mm^2 .

Industrial applicability

- 30 The invention can be used for strengthening tools made from steel, hard alloy or diamond which are used for processing materials by means of cutting or pressing.

The latter is the most promising field for applications of the proposed technology due to the absence of competing coating technologies applicable to the manufacture of press tools of complex shape for drawing wires and tubes and for extruding profile sections from aluminium, copper, steel and other metals and alloys. The carbon-tungsten coatings referred to can be deposited on tools and casting moulds used for moulding items from plastics, silicate masses and other abrasive mixtures.

The invention can also be applied for the deposition of erosion resistant coatings on turbine blades, and nozzles for water-jet cutting, surface treatment, rock washing etc.

10 The invention is promising for mechanical engineering in the production of automobiles, tractors, roadmaking machines and other mechanisms in which high wear resistance of friction components is essential. A high economic effect can be expected from the deposition of these coatings on the pressing tools (punches, dies etc.) used in mechanical engineering.

15 Many items of oil and gas equipment (ground-level pumps, immersion pumps, Christmas tree accessories etc.) can be significantly improved by means of the deposition of wear and corrosion resistant coatings obtained in accordance with this invention.

20

CLAIMS:

1. Material for wear, erosion and corrosion resistant coatings, consisting of tungsten carbide alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.
- 5 2. Material in accordance with claim 1, wherein the said material is tungsten monocarbide WC alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.
3. Material in accordance with claim 1, wherein the said material is tungsten
- 10 semicarbide W_2C alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.
4. Material in accordance with claim 1, wherein the said material is tungsten subcarbide W_3C alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.
- 15 5. Material in accordance with claim 1, wherein the said material is tungsten subcarbide $W_{12}C$ alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.
6. Material in accordance with claim 1, wherein the said material additionally contains fluorocarbon compositions with carbon content up to 15 wt% and fluorine
- 20 content up to 0.5 wt%.
7. Material for wear, erosion and corrosion resistant coatings comprising a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon
- 25 content up to 15 wt% and fluorine content up to 0.5 wt%.
8. Coating, *characterised* in that it contains:
 - an internal layer consisting of tungsten deposited on a substrate;
 - and an external layer deposited on the said internal layer and containing
 - 30 tungsten carbide in accordance with claims 1-6.

9. Coating in accordance with claim 6, *characterised* in that its outer layer additionally contains a mixture of tungsten carbides in accordance with claim 7.

10. Coating in accordance with claims 8 or 9, *characterised* in that its outer layer
5 additionally contains tungsten.

11. Coating in accordance with claims 8 or 9, *characterised* in that its outer layer additionally contains carbon.

10 12. Coating in accordance with any of claims 8 to 11, *characterised* in that its internal layer has a thickness of 0.5-300 μm and its outer layer has a thickness of 0.5-300 μm , with the ratio of thicknesses of the internal and external layers ranging from 1:1 to 1:600.

15 13. Process for producing tungsten carbides by chemical vapour deposition on a heated substrate using a mixture of gases including tungsten hexafluoride, hydrogen, a carbon-containing gas and, optionally, an inert gas, *characterised* in that the carbon-containing gas is thermally activated beforehand by heating to temperature 500-850°C.

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14. Process in accordance with claim 13, *characterised* in that the said carbon-containing gas is propane.

15. Process in accordance with claims 13 or 14, *characterised* in that it is
25 performed at a pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

16. Process in accordance with claim 15, *characterised* in that it is performed at a
30 ratio of carbon-containing gas to hydrogen 1.0-1.5 and ratio of tungsten hexafluoride

to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, tungsten monocarbide WC is obtained.

17. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.75-0.90 and ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, tungsten semicarbide W_2C is obtained.

18. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.05-0.55, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, tungsten subcarbide W_3C is obtained.

19. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.45 and ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, tungsten subcarbide $W_{12}C$ is obtained.

20. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.90-1.00 and ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, a mixture of the carbides WC and W_2C is obtained.

21. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.75 and ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated

beforehand to temperature 580-730°C; in this case, a mixture of the carbides W_2C and W_3C is obtained.

22. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, a mixture of the carbides W_2C and $W_{12}C$ is obtained.

23. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.45-0.60 and ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, a mixture of the carbides W_3C and $W_{12}C$ is obtained.

24. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.65-0.70 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, a mixture of the carbides W_2C , W_3C and $W_{12}C$ is obtained.

25. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, a mixture of the carbide WC and tungsten is obtained.

26. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated

beforehand to temperature 600-720°C; in this case, a mixture of the carbides W_2C and tungsten is obtained.

27. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, a mixture of the carbide W_3C and tungsten is obtained.

28. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.20-0.35 and ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbide $W_{12}C$ and tungsten is obtained.

29. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.60 and ratio of tungsten hexafluoride to hydrogen 0.05-0.07, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbides W_3C , $W_{12}C$ and tungsten is obtained.

30. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 1.50-1.70 and ratio of tungsten hexafluoride to hydrogen 0.10-0.12, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, a mixture of the carbide WC and carbon is obtained.

31. Process for the deposition of coatings consisting of an internal layer of tungsten and an external layer containing tungsten subcarbide $W_{12}C$ on substrates, preferably on construction materials and on items made from them, *characterised* in that the said process includes the following stages:

- (a) placing the substrate in a chemical vapour deposition reactor;
- (b) evacuating the reactor;
- (c) heating the said substrate;
- (d) supplying tungsten hexafluoride and hydrogen to the reactor;
- 5 (e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;
- (f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;
- (g) retaining the substrate in the gaseous medium formed at stage (f) for the
- 10 time necessary for the formation of the outer layer containing tungsten carbides and mixtures of them with each other, with tungsten or with free carbon.

32. Process in accordance with claim 31, *characterised* in that it is performed at a reactor pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-
15 containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

33. Process in accordance with claim 31, *characterised* in that, before the application of a coating to materials or items made from materials selected from a
20 group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical precipitation from aqueous
25 solutions, electrolysis of melts or physical and chemical vapour precipitation.

34. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 1.00-1.50 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.10, and that the carbon-containing gas is heated
30 beforehand to temperature 750-850°C; in this case, an external layer containing tungsten monocarbide WC is obtained.

35. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.75-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated
5 beforehand to temperature 600-750°C; in this case, an external layer containing tungsten semicarbide W_2C is obtained.

36. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten
10 hexafluoride to hydrogen 0.050-0.055, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, an external layer containing tungsten subcarbide W_3C is obtained.

37. Process in accordance with claim 32, *characterised* in that it is performed at a
15 ratio of the carbon-containing gas to hydrogen 0.35-0.40 and a ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, an external layer containing tungsten monocarbide $W_{12}C$ is obtained.

20 38. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.90-1.00 and a ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, an external layer containing a mixture of the carbides WC and W_2C is obtained.

25 39. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.75 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated beforehand to temperature 580-730°C; in this case, an external layer containing a
30 mixture of the carbides W_2C and W_3C is obtained.

40. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.65-0.70 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, an external layer containing a mixture of the carbides W_2C , W_3C and $W_{12}C$ is obtained.

41. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, an external layer containing a mixture of the carbides W_2C and $W_{12}C$ is obtained.

42. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.40-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ is obtained.

43. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide W_2C and tungsten is obtained.

44. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, an external layer containing a mixture of the carbide W_3C and tungsten is obtained.

45. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.050-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-690°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ with tungsten is obtained.

46. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.20-0.35 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, an external layer containing a mixture of the carbide $W_{12}C$ and tungsten is obtained.

47. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide WC and tungsten is obtained.

48. Process in accordance with any of claims 31 to 47, *characterised* in that the coatings are deposited onto frictional assemblies.

49. Process in accordance with any of claims 31 to 47, *characterised* in that the coatings are deposited onto forming tools used for processing materials by means of pressing.

50. Process in accordance with any of claims 31 to 47, *characterised* in that the coatings are deposited onto components and units of machines and mechanisms operating with compressed gases and liquids or other pneumatic or hydraulic systems.

51. Material comprising:

- a substrate made from construction material;
- a coating deposited on the said substrate, consisting of an internal tungsten layer and an external layer containing tungsten carbide alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

52. Material in accordance with claim 51, wherein the said tungsten carbide is monocarbide WC.

53. Material in accordance with claim 51, wherein the said tungsten carbide is semicarbide W_2C .

54. Material in accordance with claim 51, wherein the said tungsten carbide is subcarbide W_3C .

55. Material in accordance with claim 51, wherein the said tungsten carbide is subcarbide $W_{12}C$.

56. Material comprising:

- a substrate made from construction material;
- and a coating deposited on the said substrate, consisting of an internal tungsten layer and an external layer containing a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

57. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides WC and $W_{12}C$.

58. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and W_2C .

59. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and $W_{12}C$.
- 5 60. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C and $W_{12}C$.
61. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C , W_3C and $W_{12}C$.
- 10 62. Material in accordance with claims 52-61, *characterised* in that the external layer of the said coating additionally contains tungsten.
63. Material in accordance with claims 52-61, *characterised* in that the external
15 layer of the said coating additionally contains carbon.
64. Material in accordance with claims 52 to 63, *characterised* in that the internal layer of the said coating has thickness 0.5-300 μm and the ratio of thicknesses of internal and external layers ranges from 1:1 to 1:600.
- 20 65. Material according to claims 52 to 64, *characterised* in that the said substrate layer adjacent to the coating contains alloys with nickel content exceeding 25 wt%, e.g. Invar, Nichrome, Monel.
- 25 66. Material obtained by the process described in any of claims 31 to 47.
67. Multilaminar coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with any of claims 1 to 6.
- 30 68. Multilaminar coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with claim 7.

69. Multilaminar coating in accordance with claims 67-68, *characterised* in that the thickness of its individual layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

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70. Process for the deposition of multilaminar coatings on substrates, preferably on construction materials and items made from them, consisting of alternating layers of tungsten and layers containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten or with free carbon, said process to include the following stages:

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(a) placing the substrate in a chemical vapour deposition reactor;

(b) evacuating the reactor;

(c) heating the said substrate;

(d) supplying tungsten hexafluoride and hydrogen to the reactor;

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(e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;

(f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;

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(g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten and with free carbon; stages (d) to (g) are repeated several times in order to form alternating layers of tungsten and layers containing tungsten carbides.

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71. Process in accordance with claim 70, *characterised* in that it is conducted at reactor pressure 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

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72. Process in accordance with claim 70, *characterised* in that, before the application of a coating to materials or items made from materials selected from a

group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical precipitation from aqueous solutions, electrolysis of melts or physical and chemical vapour precipitation.

73. Process in accordance with any of claims 70 to 72, *characterised* in that the coating is deposited onto friction assemblies.

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74. Process in accordance with any of claims 70 to 72, *characterised* in that the coating is deposited onto a forming tool used for processing materials by means of pressing.

75. Process in accordance with any of claims 70 to 72, *characterised* in that the coating is deposited onto units of machines and mechanisms operating with compressed gases and liquids or of other pneumatic or hydraulic systems.

76. Construction material comprising a substrate and a multilaminar coating consisting of alternating layers of tungsten and layers containing tungsten carbide alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

77. Material in accordance with claim 76, wherein the said tungsten carbide is tungsten monocarbide WC.

78. Material in accordance with claim 76, wherein the said tungsten carbide is tungsten semicarbide W_2C .

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79. Material in accordance with claim 76, wherein the said tungsten carbide is tungsten subcarbide W_3C .
80. Material in accordance with claim 76, wherein the said tungsten carbide is tungsten subcarbide $W_{12}C$.
81. Construction material comprising a substrate and a multilaminar coating consisting of alternating layers of tungsten and layers containing a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluoride content up to 0.5 wt%.
82. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides WC and W_2C .
83. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides W_2C and W_3C .
84. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides W_3C and $W_{12}C$.
85. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides W_2C and $W_{12}C$.
86. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides W_2C , W_3C and $W_{12}C$.
87. Material in accordance with any of claims 76 to 86, *characterised* in that the said carbide layers additionally contain tungsten.

88. Material in accordance with any of claims 76 to 86, *characterised* in that the said carbide layers additionally contain carbon.

89. Materials according to any of claims 76 to 88, *characterised* in that the
5 thickness of its layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

90. Construction material obtained by any of the processes described in claims 70 to 72.

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Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

DO/PTO Rev. 6/95 DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION <input type="checkbox"/> Declaration Submitted with Initial Filing OR <input checked="" type="checkbox"/> Declaration Submitted after Initial Filing	U.S. Department of Commerce Patent and Trademark Office	Attorney Docket Number	7095HL-1
		First Named Inventor	LAKHOTKIN
	COMPLETE IF KNOWN		
	Application Number	09/913,324 ✓	
	Filing Date	August 10, 2001 ✓	
	Group Art Unit		
		Examiner Name	

As below named inventor, I hereby declare that::

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed for which a patent is sought on the invention entitled:

"TUNGSTEN CARBIDE COATING AND METHOD FOR ITS PRODUCTION"

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on
(MM/DD/YYYY)

11 February 1999 ✓

as United States Application Number or PCT International

Application Number

PCT/RU99/00037 ✓

and was amended on
(MM/DD/YYYY)

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code § 119 (a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any Pct international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				Yes	No
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
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☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto.

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below

Application Number(s)	Filing Date (MM/DD/YYYY)	
		<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

Type a plus sign (+) inside this box → ☐

DECLARATION

Page 2

I hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code § 112.1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/RU99/00037	February 11, 1999	

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☒ Firm Name OR SHERIDAN ROSS P.C. Customer Number or label
☐ List attorney(s) and/or agent(s) name and registration number below:

Name	Registration Number	Name	Registration Number
ZINGER, DAVID F.	<u>29,127</u>	HANSEN, LEWIS D.	<u>35,536</u>
GROSETH, CRAIG C.	<u>31,713</u>	KOVARIK, JOSEPH E.	<u>33,005</u>
BLAKELY, TODD P.	<u>31,328</u>	SWARTZ, DOUGLAS W.	<u>37,739</u>
CONNELL, GARY J	<u>32,020</u>	KUGLER, BRUCE A.	<u>38,942</u>
CROOK, WANNELL M.	<u>31,071</u>	BRUNELLI, ROBERT R.	<u>39,617</u>
STAVISH, SABRINA CROWLEY	<u>33,374</u>	HANSRA, TEJPAL S.	<u>38,172</u>

☒ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto

Please direct all correspondence to: ☐ Customer Number or label OR ☐ Fill in correspondence address below

Name BRENT P. JOHNSON
Address 1560 BROADWAY, SUITE 1200
Address
City DENVER State COLORADO Zip 80202-5141
Country UNITED STATES OF AMERICA Telephone (303) 863-9700 Fax (303) 863-0223

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name Jury Middle Initial V. Family Name Lakhotkin Suffix e.g. Jr.

Inventor's Signature X Lakhotkin Date 19.10.2001

Residence City Moscow State Russia Country Russia Citizenship Russia


Post Office Address ul. Seligerskaya, 10-1-63

Post Office Address

City Moscow State Russia Zip 127474 Country Russia Applicant Authority

☒ Additional inventors are being named on supplemental sheet(s) attached hereto.

Type a plus sign (+) inside this box → ☐

DECLARATION										ADDITIONAL INVENTOR(S) Supplemental Sheet																	
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor																	
Given Name		Vladimir				Middle Initial		P.		Family Name				Kuzman				Suffix e.g. Jr.									
Inventor's Signature										Date		19.10.2001															
Residence City		Moscow				State		Russia				Country		Russia				Citizenship		Russia							
Post Office Address		ul. Golubinskaya, 19-142																									
Post Office Address																											
City		Moscow				State		Russia				Zip		117574				Country		Russia				Applicant Authority			
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor																	
Given Name						Middle Initial				Family Name								Suffix e.g. Jr.									
Inventor's Signature										Date																	
Residence City						State						Country						Citizenship									
Post Office Address																											
Post Office Address																											
City						State						Zip						Country						Applicant Authority			
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor																	
Given Name						Middle Initial				Family Name								Suffix e.g. Jr.									
Inventor's Signature										Date																	
Residence City						State						Country						Citizenship									
Post Office Address																											
Post Office Address																											
City						State						Zip						Country						Applicant Authority			
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor																	
Given Name						Middle Initial				Family Name								Suffix e.g. Jr.									
Inventor's Signature										Date																	
Residence City						State						Country						Citizenship									
Post Office Address																											
Post Office Address																											
City						State						Zip						Country						Applicant Authority			

[] Further applicants and/or (further) inventors are indicated on another continuation sheet

Variable	Mean	Standard deviation	Minimum	Maximum
Age	30.0	4.0	20.0	40.0
Gender	0.5	0.5	0.0	1.0
Marital status	0.5	0.5	0.0	1.0
Education	12.0	1.0	10.0	14.0
Income	1.0	0.5	0.0	2.0
Occupation	1.0	0.5	0.0	2.0
Religion	1.0	0.5	0.0	2.0
Political party	1.0	0.5	0.0	2.0
Health status	1.0	0.5	0.0	2.0
Smoking status	0.5	0.5	0.0	1.0
Alcohol consumption	0.5	0.5	0.0	1.0
Exercise frequency	1.0	0.5	0.0	2.0
Stress level	1.0	0.5	0.0	2.0
Life satisfaction	1.0	0.5	0.0	2.0
Overall health	1.0	0.5	0.0	2.0